GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 7/6/79

Project Title: Resonance Spectra of Synthetic Metalloporphyrins

Project No: G-41-684 Green card

Project Director: Dr. Donald C. O'Shea

Sponsor: National Science Foundation; Washington, D. C. 20550

Agreement Period: From 7/1/79 Until ~~12/31/80*~~ 82 6/30/83
*Includes 6 month flexibility period.

Type Agreement: Grant No. DMR-7907758

Amount: $61,700 NSF Funds (G-41-684)
16,959 GIT Contribution (G-41-324)
$78,659 Total

Reports Required: Annual Progress Report(s); Final Project Report

Sponsor Contact Person (s):

Technical Matters
NSF Program Official
Dr. Fred E. Stafford
Program Director
Solid State Chemistry Program
Condensed Matter Sciences Section
Division of Materials Research
Directorate for Mathematical and Physical Sciences, and Engineering
National Science Foundation
Washington, D. C. 20550

202/632-7404

Contractual Matters
(thru OCA)

NSF Grants Official

Ms. Paulette L. Greene
Section I, MPE/STIA Branch
Division of Grants and Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550

202/632-5900

Defense Priority Rating: n/a

Assigned to: Physics (School/Laboratory)

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CA-3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 7/7/83

Project Title: Resonance Spectra of Synthetic Metalloporphyrins

Project No: G-41-684

Project Director: D. C. O'Shea

Sponsor: National Science Foundation, Washington D.C.

Effective Termination Date: 6/30/83

Clearance of Accounting Charges: 6/30/83

Grant/Contract Closeout Actions Remaining:

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal ~~Report~~ Accounting (FCTR)
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

Assigned to: Physics (School/~~Laboratory~~)

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FORM OCA 10:781

SUMMARY OF SCIENTIFIC PROGRESS

In the past year we have perfected a number of techniques and apparatus for deposition of large molecules in matrix isolation. The samples may now be produced reliably with a uniformity that allows reproducible results in different regions of the matrix crystal. Part of the above improvement is due to a new coaxial design for a matrix deposition oven, which deposits the matrix gas and porphyrin in a single stream increasing the uniformity of deposition considerably. The balance of the improvement is due to a definition of reliable preparation, characterization and deposition techniques which have reduced an uncertain set of procedures to routine ones and decreased background fluoresence problems markedly.

Another problem solved in the past year has been the standardization of Raman intensities. Because all previous work had been done in liquids, the normalization of Raman intensities was done by referencing them to the solvent lines, which were non-resonant. In matrix isolation work, the standards for the resonance lines were the phonon lines of the sapphire substrate. After a number of runs using the sapphire lines showed large variation in results which should have given smooth curves, we determined that there was considerable temperature dependence in the strong sapphire lines. The study details the amount of variation, provided a reliable normalization factor and has also given us an internal temperature standard which is recorded on all spectra.

Since these problems have been solved, resonance Raman spectra of copper meso-tetraphenyl porphyrin (CuTPP) have shown consistent results. Splitting in the Q(0-1) or B, band of the excitation profile has been observed and its origin is currently being investigated. A presentation of the matrix isolation technique and some results on the CuTPP is planned for the VIIth International Conference on Raman Spectroscopy in Ottawa in August 1980.

The picosecond pulse equipment requested during the first year of the grant has been ordered and a portion has been received. The process seems to be taking longer than it used to. The Tektronix 4051 graphics terminal ordered with grant monies has proven to be an efficient transmitter and modifier of data. By using a tape communications mode, we are able to read data onto the Institute Cyber 7600 for analysis and graphing. This has reduced our turn-around time considerably both for this project and two others in our laboratory. The full extent of its usefulness has not been determined yet. One limitation which has shown up, however, is the lack of memory in the Tektronix 4051 for on-site date analysis. Because of the memory management design, only small segments of the spectrum can be analyzed in a piecemeal manner. The revised budget includes money to purchase an additional 24K of random access memory to provide for analyses of entire spectra.

A replacement was sought for Dr. Jo-Lien Yang, who moved out of state. Despite phone calls, letters and an advertisement in PHYSICS TODAY, few candidates were found. The number of good people available for advanced physical research is quite limited, particularly in the field of Laser Spectroscopy. (This is also reflected in the quality of candidates for a tenure track position in this field!) I have selected Dr. Shrikrishna M. Mudare to replace Dr. Yang. Dr. Mudare took a Ph.D. under Dr. Howard Jackson at the University of Cincinnati and has a good background in experimental laser spectroscopy. He has visited the campus during the Christmas holidays and is enthusiastic about joining the effort.

STUDENT AND POSTDOCTORALS SUPPORTED

Patrick O'Rourke is a graduate research assistant on the project. He has been responsible for day-to-day data taking and analysis. He has participated in the design of the coaxial oven and has provided the major effort on the definition of deposition procedures.

Michael Neptune is a beginner graduate student working on the project as a Stelson fellow He is expanding the use of the Tektronix 4051 graphics terminal in the Raman system.

Shrikrishna M. Mudare has been hired as the new postdoctoral assistant on the project. (see above)

FUNDS ESTIMATED TO REMAIN DURING THIS YEAR

Because we could not find an immediate replacement for Dr. Yang, her portion of the funds have not been expended. The amount, however, needed to attract a good postdoctoral fellow was more than we were paying Dr. Yang. For this reason the budget for the next year is amended to show the increased expenditures. Taking into account a slight increase in the fringe benefits plus increased requests for materials and supplies and the 24 Kilobyte computer memory, the unexpended funds will cover these increases. Thus the overall request is the same as in the original budget.

SUMMARY OF SCIENTIFIC PROGRESS

During the past year the work on the matrix isolated synthetic metalloporphyrins has progressed slowly but steadily on a number of fronts. The progress may be classified into four broad areas: matrix absorption spectra, resonance Raman data analysis, resonance Raman profiles and spectroscopic techniques. The area of greatest difficulty is the interpretation of the resonance Raman excitation profiles for strongly coupled systems, as it is for others in the field.

A. ABSORPTION SPECTRA OF CuTPP

The interaction of a molecule with its surrounding tends to broaden the internal vibrational excitations causing increased intermode coupling and making it difficult for the scientist to sort out the primary coupling mechanisms from secondary and tertiary ones. It has always been the goal of this project to produce a system, which could provide this unraveling through matrix isolation because of both lowered temperatures and dilution of the molecules by the matrix. One indication of our success can be seen in Figure 1. A gas phase absorption spectrum of copper tetraphenylporphrin (CuTPP) with a Soret Band halfwidth at 22.4 nm is shown. This spectrum is difficult to achieve because of the low vapor pressure of the molecule even at elevated temperatures and the tendency of the material to deposit on optical windows despite numerous design precautions when fabricating the ovens and cells. Enclosed within this spectrum is a typical matrix isolation absorption spectrum of CuTPP. It can be seen that the peak of the Soret Band is at the same frequency as the gas phase spectrum, a good indication that the sample has, indeed, achieved the "gas phase approximation" we had hoped for. In addition, the width of the Soret Band at half-maximum is considerably narrower than any absorption spectra of other porphyrins in other environments. In matrix isolation the half width of the Soret Band is 5.6 nm,

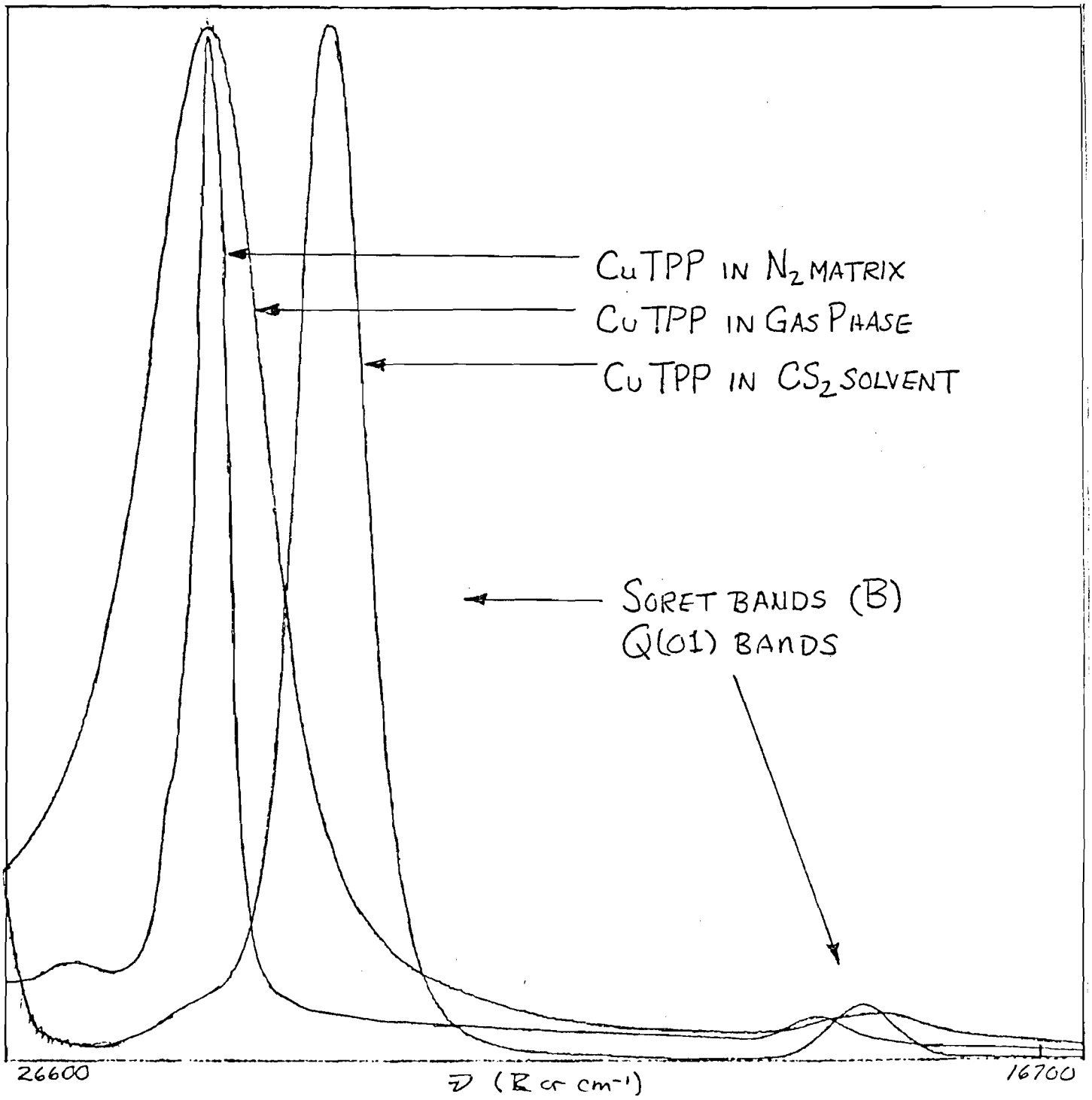

CuTPP IN N_2 MATRIX
CuTPP IN GAS PHASE
CuTPP IN CS_2 SOLVENT
SORET BANDS (B)
Q(01) BANDS
26600
$\bar{\nu}$ (R or cm^{-1})
16700

FIGURE 1

and most solution spectra, also plotted in Figure 1, show line widths in the neighborhood of 14 nm. Whether this is the smallest achievable line width is not known. A series of experiments will be run with other rare gases and SF_6 to try to determine this. If these spectra are compared to standard solution spectra it is seen that the vibronic side bands show some structure - something that has never been seen in solution spectra. This opens the possibility for selective excitations into sections of the vibronic manifolds.

B. RAMAN SPECTRA DATA ANALYSIS

One of the difficulties with resonance Raman excitation experiments is the internal standard which is used to compare one spectrum to another to build up the profiles. We had tried using the Raman lines of the sapphire substrates and adjusting for any temperature dependence by examining the ratios of the substrate lines, but this proved unsatisfactory over many runs and different matrix crystals. We have developed a new technique to provide a standard independent of the substrate. All data is now analyzed using the matrix vibrational line. In this case, the 2330 cm^{-1} of nitrogen. Initially this had not been used because of the large frequency separation between this line and most of the other Raman lines in the region 400 to 1600 cm^{-1}. This was solved by using a black body radiator to standardize the response of the optics-spectrometer-detector system. A single response correction curve has been generated that applies the correct normalization factors to all lines in the spectrum before intercomparison.

Another difficulty that has been solved is an acceptable technique for smoothing data and removing noise, especially in those regions where the resonance is weak. Through the use of a correlation program which correlates seven points on the N_2 standard line with seven points in the spectrum, a

considerable improvement in signal to noise has been made without any rounding of the signal peaks. The whole process has been enhanced by a Fourier transform ROM pack purchased with grant funds for our Tektronix 4051 microcomputer.

C. RESONANCE RAMAN EXCITATION PROFILES

The wealth of lines in these spectra is considerable. There are at least 80 reproducible lines of which 20 remain strong and interesting over a wide enough region to be studied. A partial resonance Raman excitation profile is shown in Figs. 2(a) and (b). These are preliminary data, designed to show the differences between these matrix isolation spectra and previous experimental attempts. No interpretation can be given yet and there is still additional spectra to be taken to assure the completeness of the details.

D. NEW EXPERIMENTAL TECHNIQUES

The laser excitation in the region of 3850 $\mathring{A}$ to 4200 $\mathring{A}$ will be very useful to probe the Soret Bank in CuTPP. We are presently working on this part of the research project. The 5245 $\mathring{A}$ line of a argon ion laser has been mode locked to produce pulses with a typical pulse width of $\sim$ 200 psec. and a repitition rate of $\sim$ 96 MHz. A dye laser is synchronously pumped by extending the dye laser cavity and by introducing an optical delay line to match the pump laser cavity. The continuous, average output of the synchronously pumped dye laser is measured to be $\sim$ 110 mw and is believed to have a pulsewidth in the range of $\sim$ 5-10 psec. All of the above work has been completed and is found to work satisfactorily.

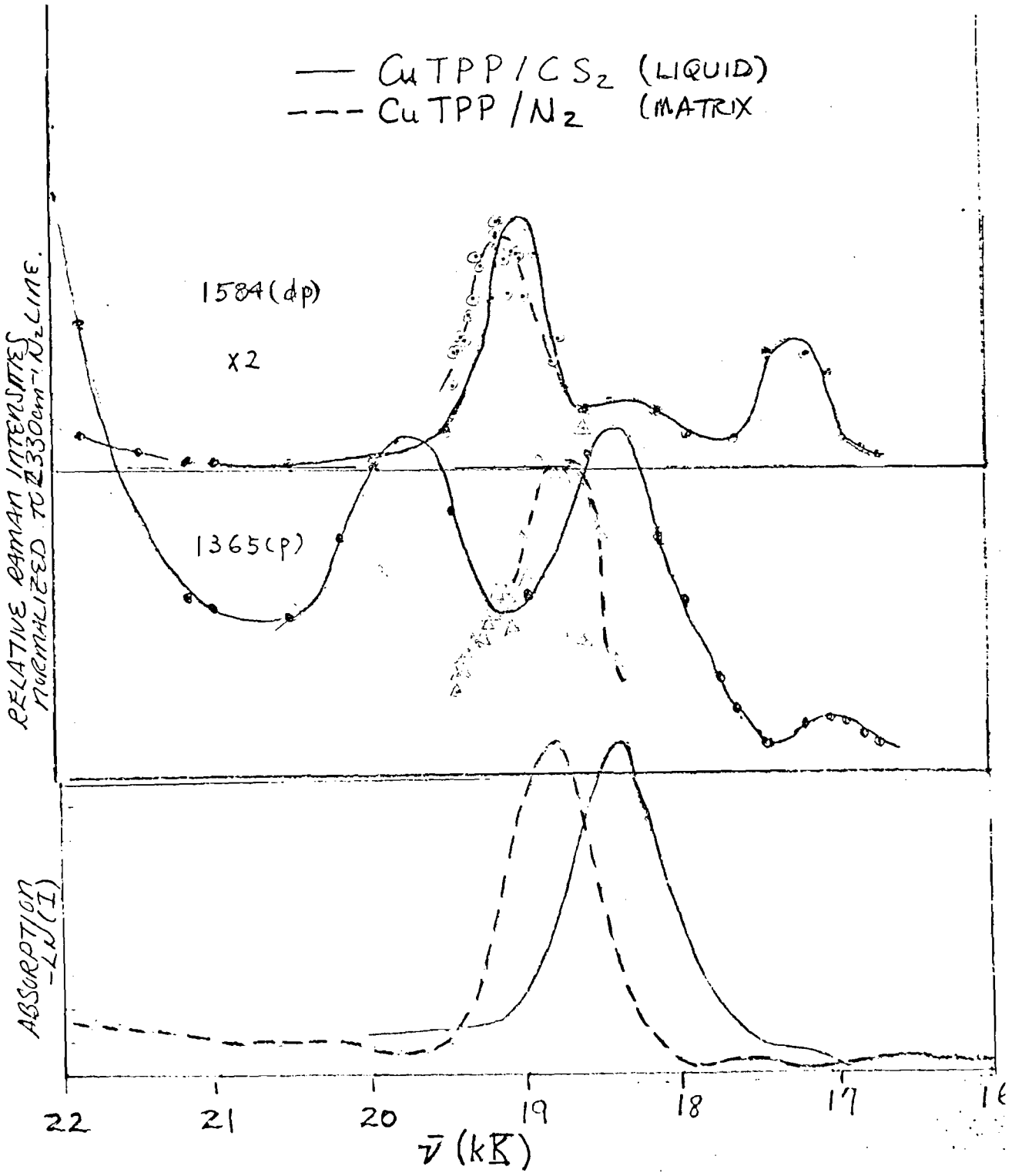

CuTPP/CS2 (LIQUID)
CuTPP/N2 (MATRIX
1584(dp)
X2
1365(p)
RELATIVE RAMAN INTENSITIES NORMALIZED TO 2330cm-1 N2 LINE.
ABSORPTION -LN(I)
22
21
20
19
18
17
ν̄ (kK)

Fig 2(b)

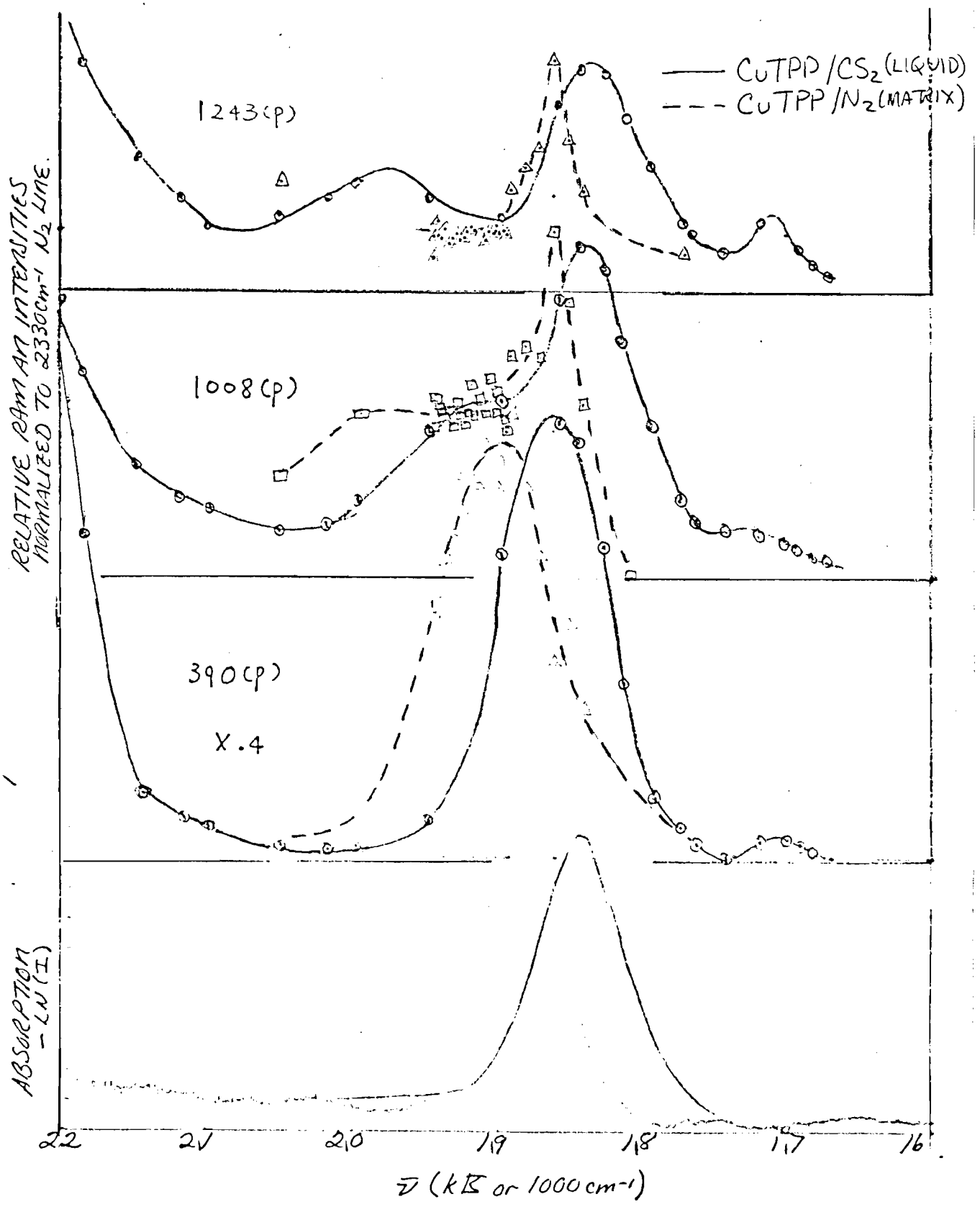

CuTPP/CS2 (LIQUID)
CuTPP/N2 (MATRIX)
1243(P)
1008(P)
390(P)
X.4
RELATIVE RAMAN INTENSITIES
NORMALIZED TO 2330cm-1 N2 LINE.
ABSORPTION
-LN(I/I0)
22
21
20
19
18
17
16
ν̄ (kK or 1000 cm-1)

Fig 2 (a)

Presently we are working on frequency doubling the synchronously pumped dye laser output by using a KDP crystal, cut for angle turning. This not only will enable us to obtain u.v. in the range of 3250 - 2850 nms (for R6G) with picosecond pulse of repetition rate (96 MHz) but also provide the exact pulse width measurements.

With the perfection of the frequency-doubling technique for Rhodamine 6G we intend to use a "piggyback" technique to pump a series of dyes to produce laser fluoresence in the region of 750 to 850 nm and thus may be frequency-doubled in the range 375 to 425 nm. Provided the peak power density is in the range of 100 - 500 kw/cm^2 the synchronously pumped dye laser should enable us to obtain picosecond pulses ideally suited for probing the Soret region of porphyrins.

STUDENTS AND POST-DOCTORALS SUPPORTED

Dr. Shrikrishna M. Mudare has been a post doctoral assistant for nearly a year now. He is responsible for the development of experimental techniques, particularly in the mode locking and frequency doubling area.

Patrick O'Rourke is the graduate research assistant on the project. He has developed a beautiful matrix isolation technique we have used these past two years. He will be finishing his graduate work this academic year. His thesis will be based on the matrix isolation of strongly-coupled synthetic metalloporphyrins.

Christopher Johnston is a graduate research assistant who is just beginning graduate work. He has done some work on evaluation of experimental techniques for ultraviolet mode-locking pumping.

Wendy Ellerbe, an undergraduate at Vanderbilt, will spend her summer working with our group as a research assistant.

PROJECTED EXPERIMENTS

With the successful solution of a number of problems, we can exploit our techniques in a number of areas. First, among these a study of different matrices to determine the true effect of these matrices on this porphyrin. We also intend to do a careful study of any orientation and polarization effects that might indicate preferential orientation of the porphyrins in the substrates. If any such effect were found, techniques for enhancing it would be investigated. To be able to hold a complicated molecule in a particular orientation with little or no environmental effect is a delightful prospect. Finally there is a need for comparison and contrast of the profiles of this porphyrin with other strong porphyrins to provide additional clues to the understanding of strong coupling.

FUNDS ESTIMATED TO REMAIN DURING THIS YEAR

Because one of the graduate students, Patrick O'Rourke is now paid on a work-study program within the last month, some encumbered funds have become free. Other funds taken together will leave $6150. This will be offset in the requests in next years budget for our argon ion laser tube. Its cost has increased enormously since this grant began. The overall request is the same as that budgeted for the entire request.

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332
(404) 894-5201

SCHOOL OF PHYSICS

September 24, 1981

MEMORANDUM

TO: National Science Foundation
Division of Materials Research
Washington, D. C. 20550

FROM: Georgia Institute of Technology
Atlanta, Georgia 30332
Principal Investigator: Dr. Donald C. O'Shea DOS

SUBJECT: Grant No: DMR 7907758
Starting Date: 7/1/79; Completion Date: 12/30/82
Grant Title: "Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphyrins"

ITEM: Annual Progress Report

I. Scientific Description of Research and Results

During the past year we have completed an extensive investigation of copper tetraphenylporphyrin (CuTPP) in rare gas and SF_6 solid matrices at 20°K using visible absorption spectroscopy and Resonance Raman spectra. While conducting these investigations we have perfected our matrix deposition technique to where we can produce optically clear samples with the same visible and Raman spectra. Lifetime of these samples, which are maintained using a closed cycle helium refrigerator, is more than three weeks. At the same time, we have improved our data collection and analysis techniques using a Tektronix 4051 graphics terminal, enabling us to analyze and reduce a spectrum with nearly one hundred peaks to a standard format listing of their frequencies and integrated intensities for use in producing Raman excitation profiles.

Because of the difficulty of inserting the sample chamber in a conventional absorption spectrometer, a single beam absorption technique has been devised which uses the Raman spectrometer system to record reference and sample transmission spectra. After measuring the relative frequency response of the system using a blackbody source, the ratio of transmission intensities with the frequency response correction are computed and plotted to give a standard absorption spectrum. The dynamic range of the system is over 50.D. and the resolution can be as high as 1 cm^{-1}.

Examples of the spectra recorded by this method are shown in Figure 1. These are absorption spectra of CuTPP in a vapor and in two rare gas matrices, argon and krypton and in a nitrogen matrix. These spectra raise questions as to the effect of temperature and solvents on the electronic states of a molecule. For example, the strong high frequency (B) band has the same center frequency for the vapor phase as the low temperature sample in an N_2 matrix, where as the weak low frequency (Q) band moves to lower frequencies with increased temperature. Also noteworthy in this series of spectra is the increase in the intensity of the low frequency (Q) band as the mass of the matrix material is increased. Of particular interest is the additional band at low frequency that appears in the spectrum of CuTPP in a SF_6 matrix. (Fig. 2). In this case an additional band, due to an extremely weak dipole transition, begins to gain intensity as the simple symmetry states of the porphyrin are mixed. This CuTPP (SF_6) system will be a useful system for future study because it allows us to "turn on" a small perturbation in this well-behaved system and study the effects on the Raman scattering intensities, allowing us to verify predictions of a simple adiabatic theory of light scattering from porphyrins.

On the basis of comparison of vapor and matrix isolated spectra it is clear that the N_2 isolated matrix provides the closest approximation to the gas phase of any of these matrices. This is based on the fact that the Soret band has the same center absorption frequency in both the N_2 matrix and in vapor phase. The Q band is at a higher frequency in the vapor than in the matrix, but this is a temperature effect that has been seen, but not explained, in other media and with other samples.

Using N_2 matrix as the environment of choice we have carried out a systematic series of investigations of CuTPP in N_2 at 20 K over a wide range of excitation wavelengths covering both the Q(0-0) and Q(0-1) bands. While a number of excitation profiles show considerable strength over a broad range of frequencies throughout the Q(0-1) excitation region, there appears to be additional structure within these broad bands. (Figure 3). In all work to the present we have never seen any sharp structure in an excitation profile. In addition, this structure is not mirrored in the absorption spectra despite attempts to observe it. This structure appears to be reproducible and not sample dependent. Further work is being done to obtain more data.

One of the problems encountered in taking the Raman data is the uncertainty in the excitation wavelength. While the wavelengths for the lasing lines of an argon ion laser are certain, much of the work involves a tunable dye laser whose output is uncalibrated. We cannot rely on the Raman spectrometer because of backlash and inaccuracies in the gears. To solve this problem we have embarked on a laser wavemeter development program. A summer research assistant, Wendy Ellerbee, a student of Vanderbilt, was responsible for development of a wavemeter based on a Michelson interferometer. One mirror of the interferometer is a corner cube reflector mounted on a toy train. By counting the number of fringes per unit distance for the unknown wavelength and a He-Ne laser, the ratio of wavelengths can be computed by a simple counter.

Another effort which is progressing in the laboratory is an alternative method to produce blue laser excitation with our present resources. We will replace the Brewster prism in our argon ion laser system with a Brewster plate (a parallelipiped with edges cut to Brewster's angle for low laser transmission loss). By using this non-dispersive plate as a modelocker in the ultraviolet, we intend to synchronously pump a blue dye. While the power output will be modest, the peak powers should be substantial and the resonance gain because the excitation would be into the strongly absorbing Soret region would be large.

These studies have opened up questions of the effect of environmental effects on the absorption spectra of these large molecules. There would appear to be certain simplifications that can be made in the study of a 50-50 mixed state porphyrin like CuTPP. We believe we may have a handle on an explanation of the broad resonance profiles that are present even at low temperatures. The narrow structure is puzzling and warrants additional study.

II. Publications

1. "A System for Resonance Raman and Visible Absorption Spectroscopy of Matrix Isolated Sample", by D. C. O'Shea, S. M. Mudare and P. E. O'Rourke (to be delivered to the Optical Society of America, October 30, 1981, paper in preparation).

2. "Visible Absorption Spectroscopy of Copper Tetraphenylporphyrin in Vapor and Matrix Isolation", D. C. O'Shea, P. E. O'Rourke and S. M. Mudare (Abstract prepared for San Francisco Joint Meeting of the APS/AAPT, January 1982).

III. Theses

"Raman Excitation Profile of Copper Tetraphenylporphyrin in a Nitrogen Matrix", Patrick Edward O'Rourke, Georgia Institute of Technology, Ph.D. Thesis (1981).

IV. Scientific Collaborators

Dr. Shrikrishna M. Mudare, Research Scientist, School of Physics.

V. Comments

We intend to seek renewal to extend these investigations to a series of porphyrins using the N_2 matrix.

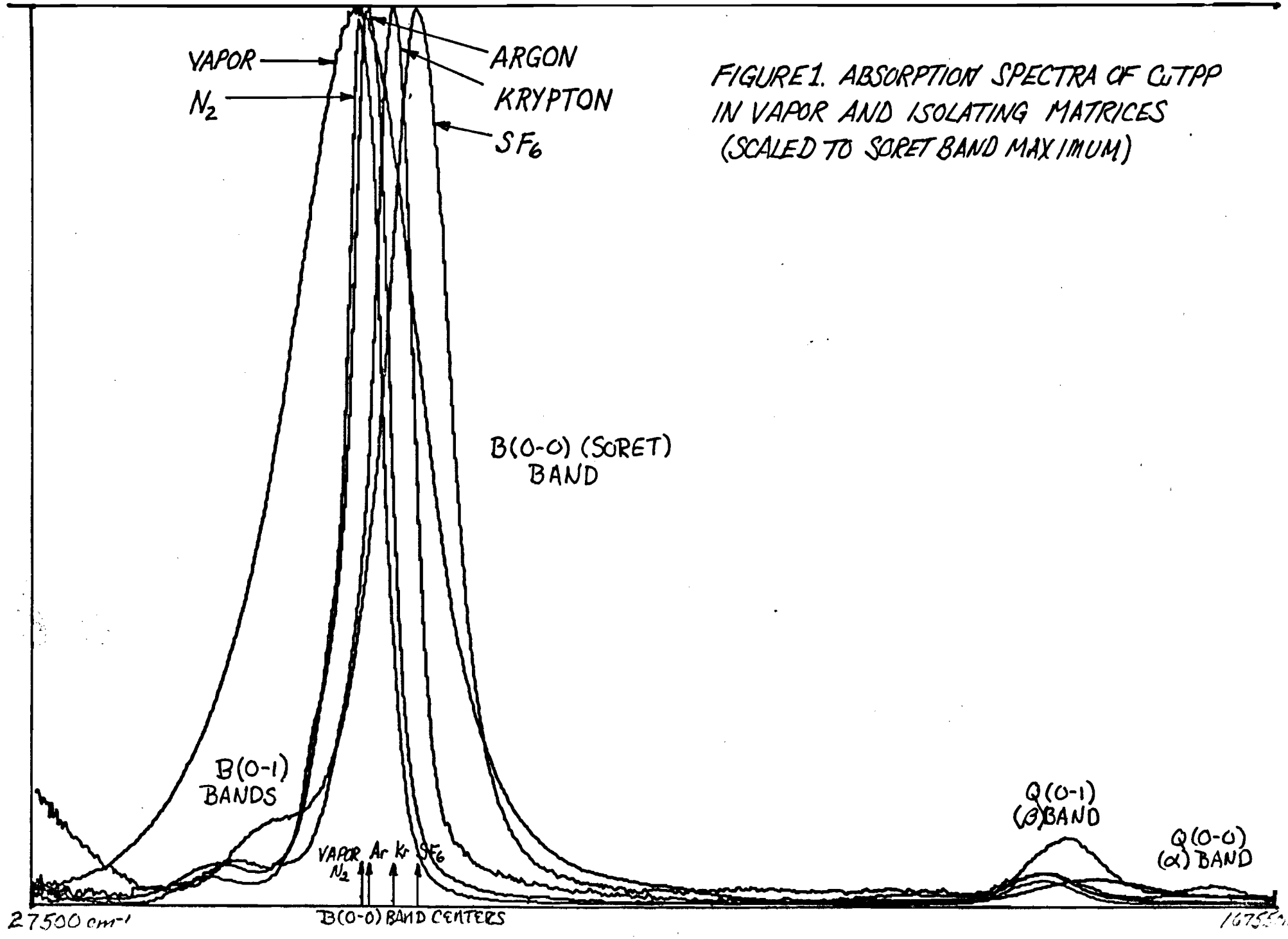
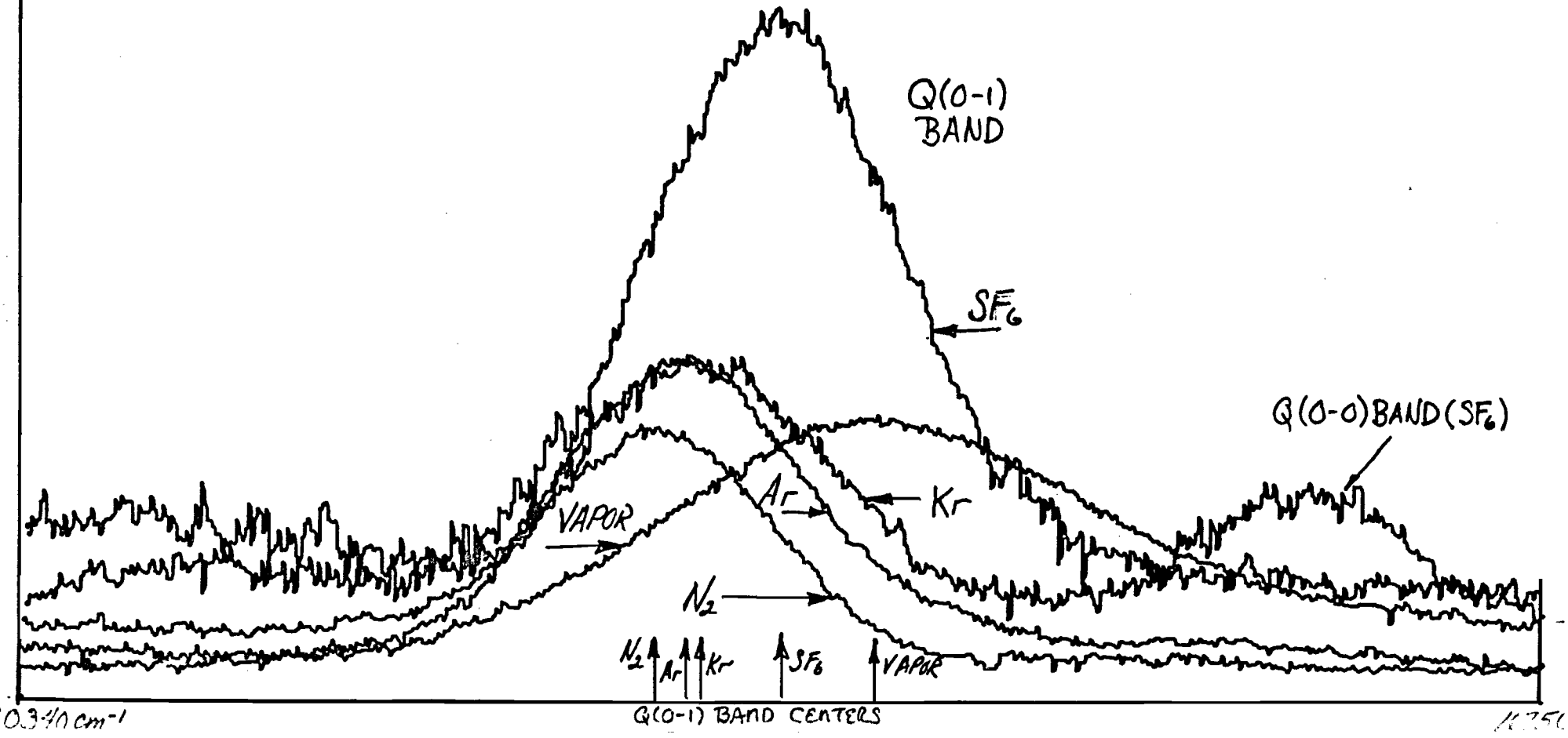


FIGURE 1. ABSORPTION SPECTRA OF CuTPP IN VAPOR AND ISOLATING MATRICES (SCALED TO SORET BAND MAXIMUM)

FIGURE 2. ABSORPTION SPECTRA OF CuTPP IN VAPOR AND ISOLATING MATRICES - Q BAND REGION (SCALED TO SORET BAND MAXIMUM)



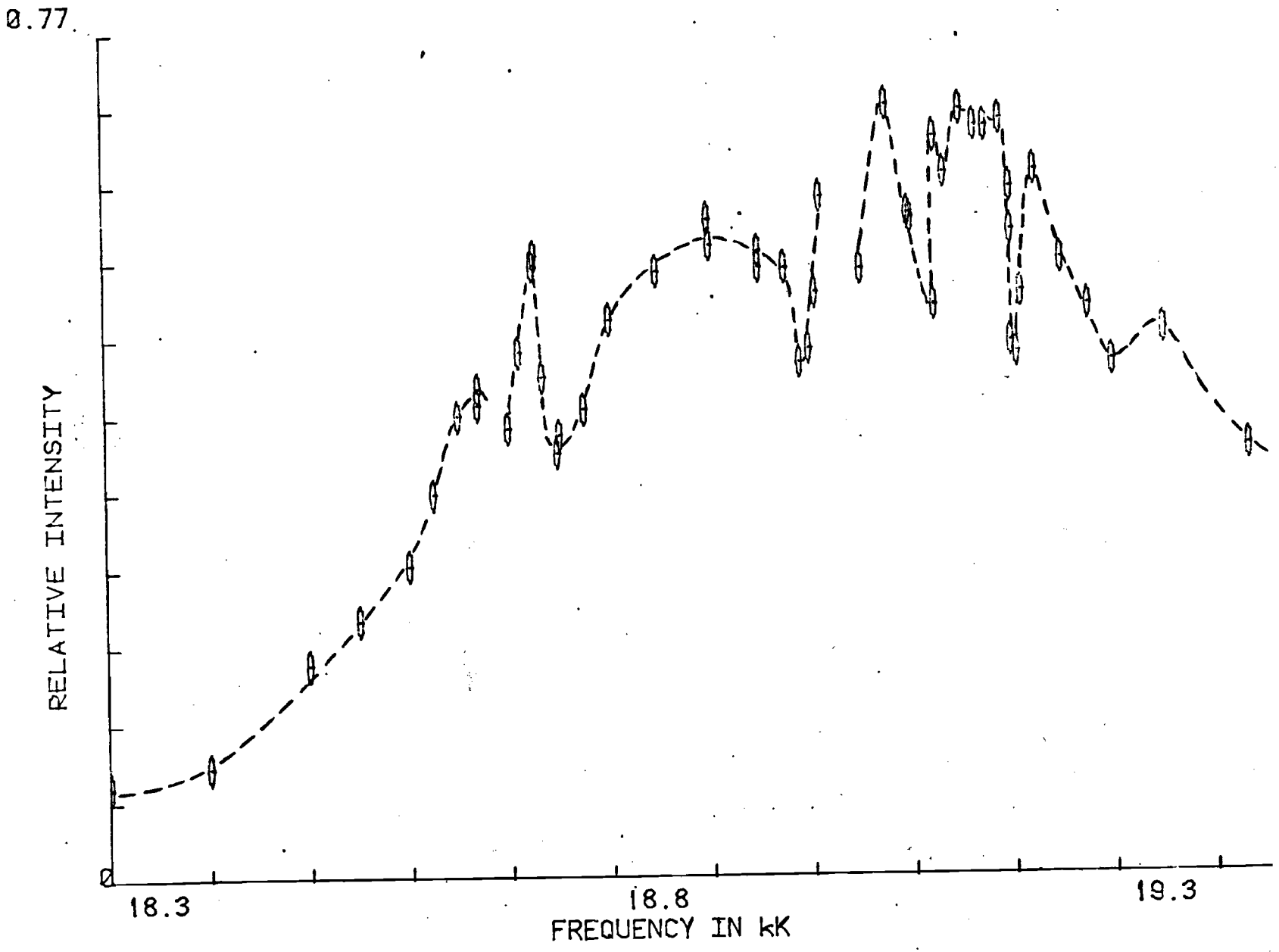

RAMAN EXCITATION PROFILE FOR LINE 393 OF CuTPP IN N2
0.77
RELATIVE INTENSITY
0
18.3
18.8
19.3
FREQUENCY IN kK

FIGURE 3

G-41-684

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology 225 North Ave., N. W. Atlanta, Georgia 30332	Materials Research	79-07758
	4. Award Period From 7/1/79 To 6/30/83	5. Cumulative Award Amount

6. Project Title

Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphyrins.

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

This project investigated the electronic structure of molecules of biological interest because of their similarity to the absorbing molecules that carry oxygen in the blood (hemoglobin) or convert sunlight to chemical energy in plants (chlorophyll).

The tool used to probe these molecules was resonant Raman scattering. A small amount of the laser energy incident on a solution of these molecules will be shifted in color by the internal atomic motions of the molecules. By detecting and analyzing this shifted radiation, one can gain some knowledge of these internal motions. When the exciting laser radiation is of a color absorbed by the molecules, the light is said to be resonant with certain molecular electronic states. In resonance, there is an enormous increase in the scattered light and a change in the relative intensities of between the various shifted color bands.

This project has advanced our understanding of the electronic states of the molecules under study by providing both experimental data and theory on the variation in shifted color intensities as a function of incident laser color (resonant Raman excitation profiles). Analyses of the Raman spectra have shown that it is not possible to decouple the motions of the electrons from the motions of the atomic nuclei when describing the energy states of these molecules. One of the most important findings was that molecular vibrations of considerably different oscillation frequency contribute to the scattering by other vibrations. We have termed these vibrations "helping modes".

Work on a copper prophyrin has indicated that there is a very strong coupling between an electronic state of the molecule and the vibrational states of the molecule. This can be compared to earlier work in which the coupling was much weaker. To study this coupling further Raman excitation profiles in a nitrogen matrix were constructed from 152 Raman spectra collected throughout the Q band region. Absorption spectra of CuTPP in six different matrix materials were also collected to assess the effects of environment on the molecule. A Born-Huang non-adiabatic perturbation theory was derived for porphyrins which can explain the strong coupling behavior exhibited by this data. It was found that the third order terms in the Raman scattering tensor are responsible for the strong coupling effects. This occurs not because the third order terms are abnormally large, but because the first and second order Q band scattering terms are very small for CuTPP.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		✓			
b. Publication Citations		✓			
c. Data on Scientific Collaborators		✓			
d. Information on Inventions	✓				
e. Technical Description of Project and Results		✓			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
DONALD C. O'SHEA		5-MAY-83.

April 15, 1983

MEMORANDUM

TO: National Science Foundation
Division of Materials Research
Washington, D. C. 20550

FROM: Georgia Institute of Technology
Atlanta, Georgia 30332
Principal Investigator: Dr. Donald C. O'Shea

SUBJECT: Grant No: DMR 7907758
Starting Date: 7/1/79 Completion Date: 6/30/83
Grant Title: "Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphyrins"

ITEM: Annual Progress Report

I. Scientific Description of Research and Results

SUMMARY OF SCIENTIFIC PROGRESS

In early work[1,2] supported by this grant we used resonance Raman spectroscopy (RRS) to obtain electronic assignments for bands in the absorption spectra of some of the hyperprophyrins. In this investigation we obtained the first experimental verification of a non-adiabatic vibronic coupling contribution to RRS intensities which was predicted by an extension[3] of the existing theory of RRS. We further demonstrated that totally symmetric modes in metalloporphyrins (previously thought to be vibronically inactive) were involved in vibronic coupling of non-degenerate electronic states. This study of Mn(III) porphyrins at room temperature showed that Raman excitation profiles (REPs) over a large range of exciting frequencies can provide valuable quantitative structural, vibrational, and electronic information not obtainable by other methods.

This investigation also pointed to deficiencies in the theoretical description of resonance Raman intensities in polyatomic molecules. In addition to the omission of the non-adiabatic terms in the scattering tensor

by previous authors, it was noted that the effects of degenerate electronic states had been omitted in theoretical treatments. The importance of the theoretical studies were enhanced when excitation profiles of nickel etioporphyrin were obtained throughout the visible.[1] REPs of the totally symmetric and Jahn-Teller active modes showed unexpected behavior indicating that the effects of degeneracy of the resonant excited electronic states had to be included in the theory. An additional anomaly observed in copper and chromium tetraphenylporphyrins (CuTPP and Cr(III)TPPCI) was the behavior of the low frequency 392 cm^{-1} symmetric mode, which shows strong Raman scattering in the Q(0-1) band at $E_{Q+1500cm^{-1}}$ and not at $E_{Q+392cm^{-1}}$ as might be expcted.[5]

To further this investigation of these molecules, matrix isolation techniques were developed at the beginning of the past three year grant period and have been refined during that time. At the present time we are able to grow and maintain crystals of rare gases, N_2, and SF_6 for periods up to one month. We are able to dope these crystals uniformly with usable molar dilutions of 10^6:1 to insure isolation of these large molecules. To characterize these samples, assuring their initial and continued integrity during the course of the run, we devised an in situ method for measuring the near ultraviolet and visible absorption spectrum of a matrix-isolated sample. This technique uses the Raman spectrometer system as a single beam absorption with a dynamic range greater than 5.0 O.D.[6]

These absorption spectra have provided not only a check on sample integrity, but have also given us an indication of the effectiveness of the matrices as molecular isolators. In Figure 1 is shown a series of absorption spectra recorded with this technique. Comparison of the strong Soret band (B band) in the vicinity of 400nm shows that the N_2-isolated CuTPP at 25K has the same band center frequency as the same band in the vapor phase spectrum at

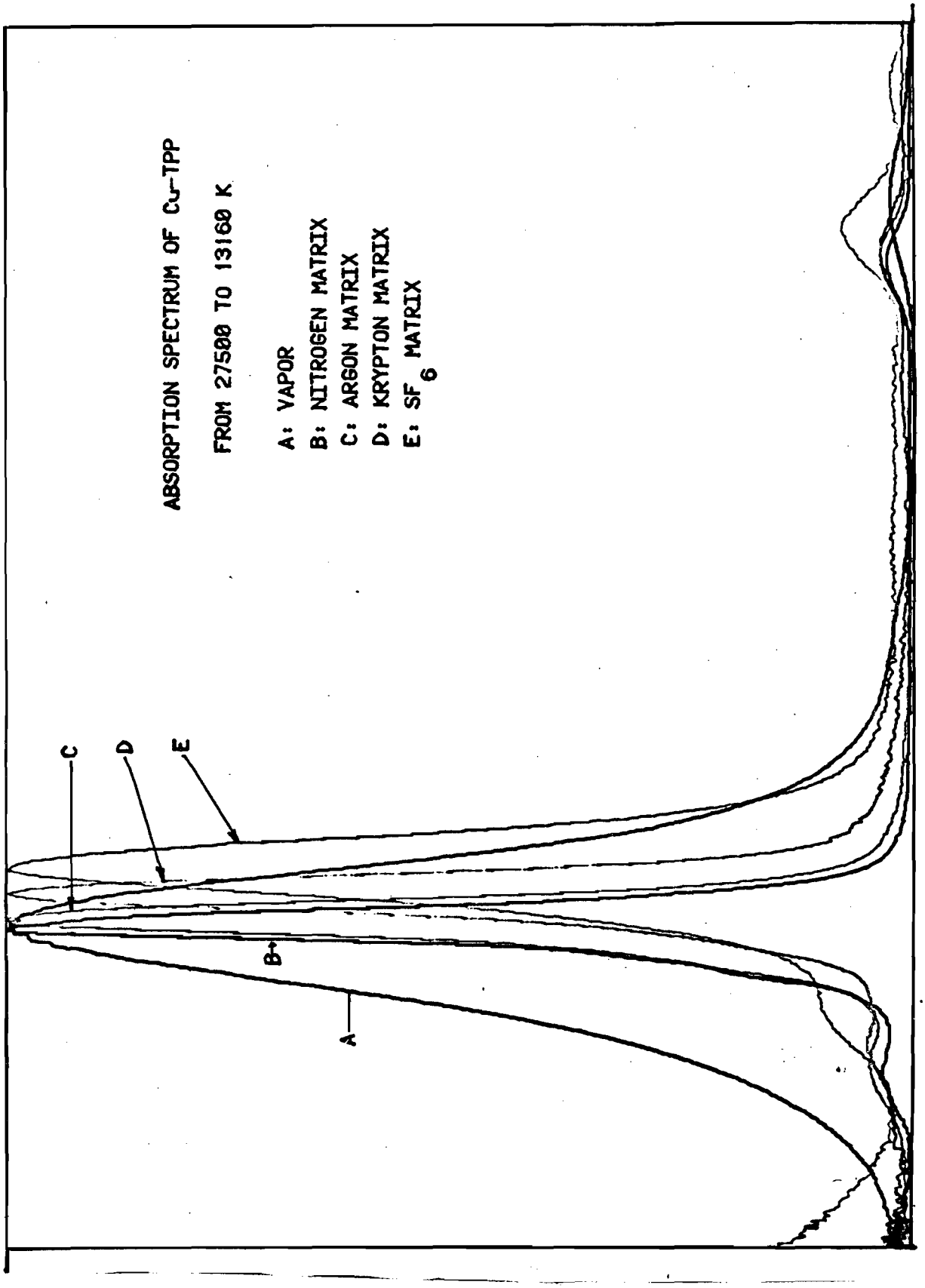


Fig. 1A. Absorption spectra of CuTPP in vapor phase and nitrogen, argon, krypton, and sulfur hexafluoride matrices from 27.5 kK (364nm) to 13.16 kK (760nm).

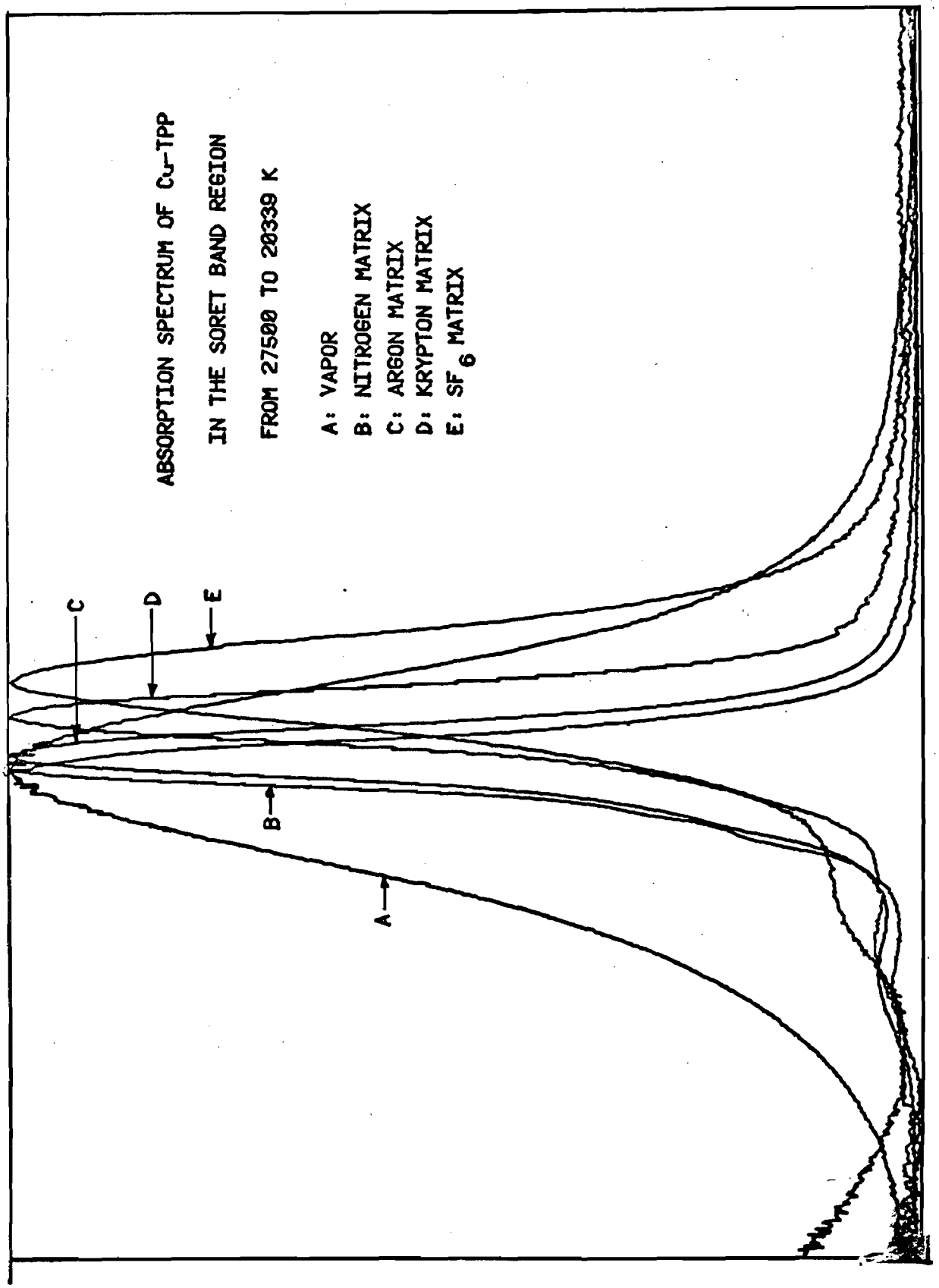


Fig. 1B. Absorption spectra of CuTPP in vapor phase and nitrogen, argon, krypton and sulfur hexafluoride matrices in the Soret band region from 27.5 kK (364nm) to 20.34 kK (492nm).

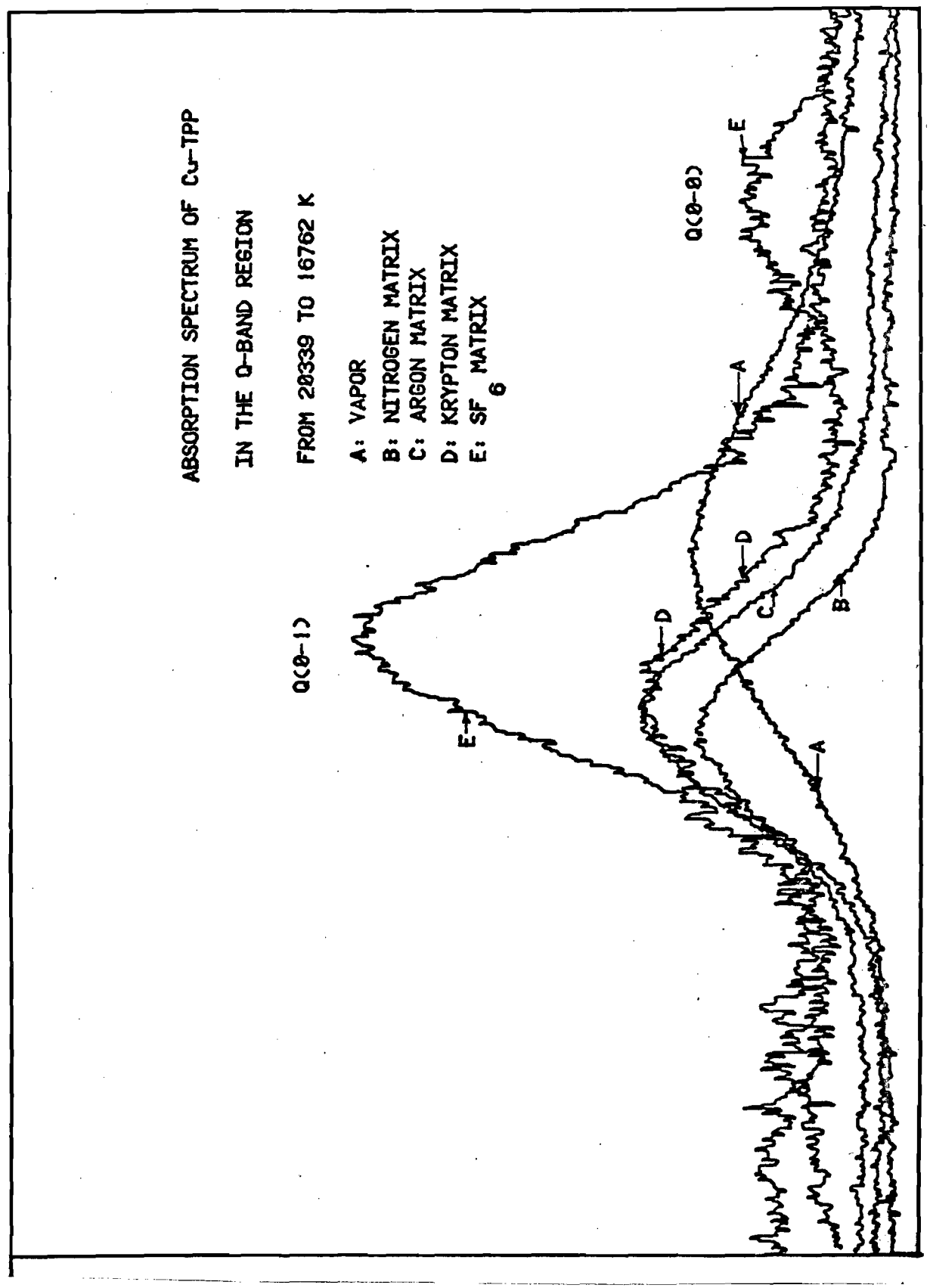


Fig. 1C. Absorption spectra of CuTPP in vapor phase and nitrogen, argon, krypton and sulfur hexafluoride matrices in the Q-band region from 20.34 kK (492nm) to 16.76 kK (597nm).

675K. All other matrices show a small Soret band shift. The shift of the Q band (the weak band around 570 nm) to longer wavelengths at high temperatures is a phenomenon that has been reported earlier for this sample and others in silicone oil at room temperature and 300° C.[7] In those experiments the Soret band did not shift with a temperature increase, while the Q band followed the same temperature dependence that we have observed. Equally noteworthy is that the temperature coefficient of the shift is $-0.8cm^{-1}/K$ in the silicon oil experiment, which is comparable to the $-0.75cm^{-1}/K$ calculated from our experiments over a considerably larger temperature range. This decrease of energy of a molecular state with increasing temperature is puzzling. Because the initial Q-B splitting is caused by configuration interaction, it is unlikely that temperature variations could change both the configuration interaction energy, $(E_B-E_Q)/2$ and the band average energy, $(E_q+E_B)/2$ in such a manner as to leave E_B constant. This leads one to the conclusion that the Q band is interacting with additional energy levels at the higher temperatures so as to reduce the energy of the Q band. Since porphyrins are enormously complicated molecules, there are a large number of unobserved levels (perhaps high order vibrational levels of the ground state manifold) that could interact with this electronic band. Since this is a general phenomenon among porphyrins, this matter warrants further study. One additional feature to be noted in the N_2 matrix absorption spectrum is a side band of the Soret band about $400cm^{-1}$ to the high energy side. Note there is no corresponding strong band present in the Q(0-1) band, the vibronic sideband to Q(0-0).

Besides the unusual behavior of the $392cm^{-1}$ mode mentioned earlier,

CuTPP is an excellent sample for study since the mixing of the basis states before configuration interaction is almost exactly a 50/50 mixture. (The ratio of I_Q/I_B is less than 1/500.) This simplifies both computational and physical arguments that must be made when interpreting the Raman and absorption spectra. Through the use of a combination of dyes for a tunable dye laser and the argon ion laser lines, we have taken Raman spectra across the Q(0-0) and Q(0-1) bands of CuTPP. We believe these spectra have enabled us to produce the most detailed Raman excitation profiles of matrix isolated samples ever recorded.

As is evident from the profile, the amount of data needed to produce the details is considerable and because of the finite lifetime of the samples due to a slow deterioration of the surface, this data must be acquired and processed as rapidly as possible. During the grant period the system has been upgraded from one in which all data smoothing and analysis was done by hand to one that provides rapid storage and analysis of data, reduction of results and plotting of the excitation profiles.[6] One of the major difficulties to be overcome in constructing the excitation profiles of a matrix-isolated substance was the establishment of a reliable internal standard. Because the optics, laser power and beam position vary slightly from run to run, plotting the Raman line heights from spectrum to spectrum is an unreliable method of generating excitation profiles no matter how carefully all experimental factors are controlled. In solution systems there are always non-resonant solvent lines that can be used as internal intensity standards for normalization. Early efforts to use the phonon lines of the sapphire substrate, which were in the center of the region of interest, as standards failed because the requirements for a high optical speed light collection system conflicted with the reduced depth of focus which such a system imposes.

That is, it was not possible to focus the sample and substrate onto the slit simultaneously without stopping down the system so far that the expense in data collection time was intolerable. Our only recourse was to use the nitrogen matrix as an alternate standard, but, unfortunately, the symmetric stretch mode at 2330cm^{-1} is far from the exciting line and most of the Raman lines of interest. To correct for the spectral response of the optics, spectrometer and photodetector, a correction curve was measured using a blackbody radiation source as a standard.[6] This curve stored in the computer is applied to each point on the REP before it is plotted. We feel that the line intensities above 5% of the N_2 are reliable data points at the present time. Work is underway to reduce this figure.

As noted earlier, the most interesting mode in the Raman spectrum is the 392cm^{-1} A_{1g} mode,[6,7] which does not peak at 392cm^{-1} from the Q(0-0) band but in the vicinity of 1500cm^{-1} from there. Recently Zgierski and Pawlikowski[8] have put forward an explanation that this is due to strong mixing of this low frequency mode with modes of high frequency that are more strongly vibronically active. We independently confirm these conclusions. Independent theoretical calculations of absorption and polarizability terms using adiabatic wavefunctions have indicated that corroborating information on the strength of these couplings exist in the line intensities of the Raman spectra in the Q(0-0) and B(0-0) bands. The excitation profile for CuTPP in N_2-matrix isolation for the 392cm^{-1} mode is shown in Figure 2. The profile does indeed peak at approximately 1500cm^{-1}.

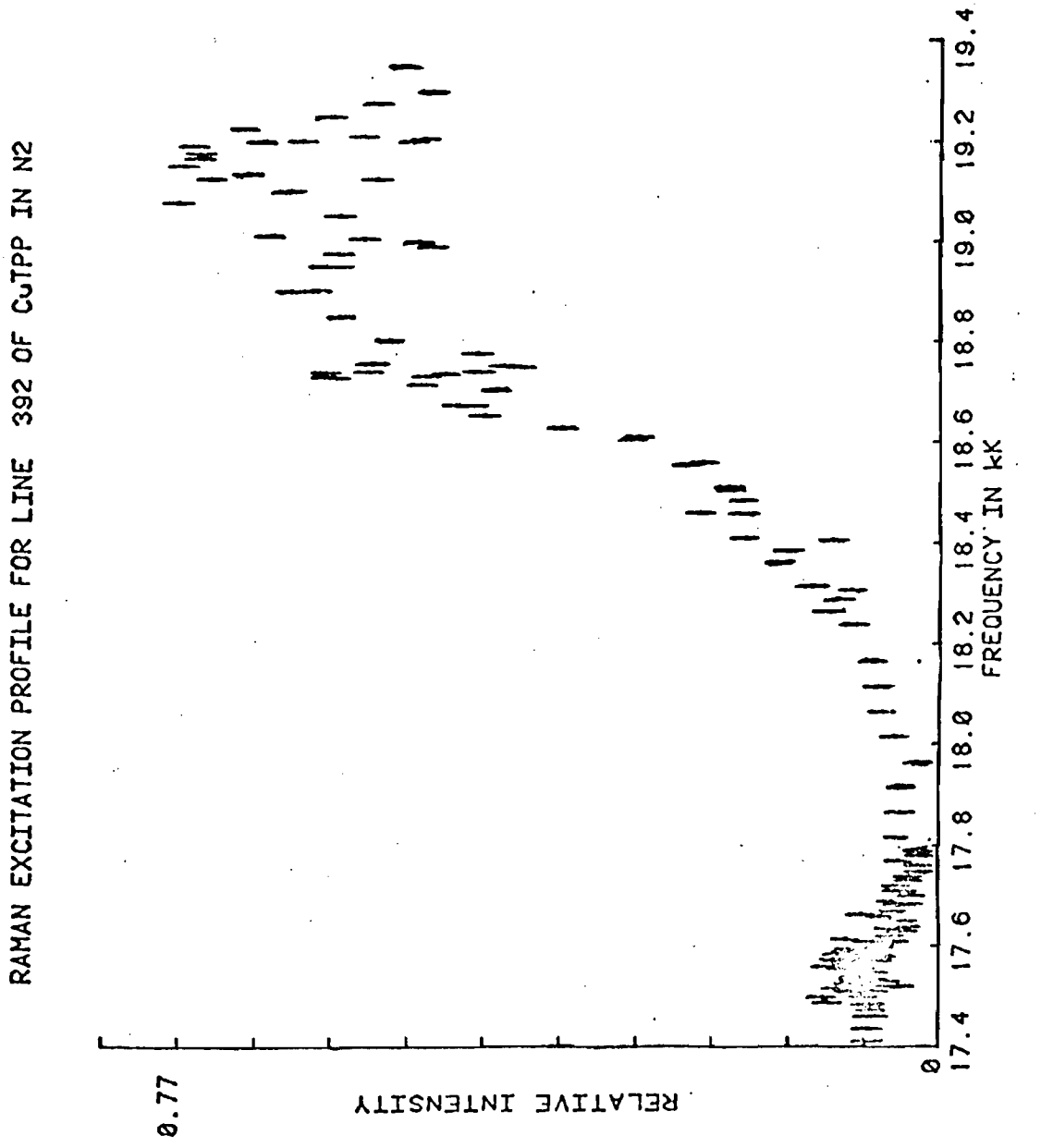


Fig. 2. Raman excitation profile of the 392cm^{-1} mode of CuTPP.

The interpretations of these data by Zgierski and Pawlikowski, we believe, is correct as far as it goes. However, for those molecules for which there is little or no unmixing of the pure 50/50 Gouterman[9] basis states, further understanding can be gained from a straightforward application of adiabatic wavefunctions to the absorption and polarizability expressions. Using these wavefunctions we find that the important terms in calculating the absorption and Raman line strengths are not the Albrecht A and B terms even with non-adiabatic correction. These terms are bilinear in dipole strengths, $M_B M_Q$, whereas the important scattering terms for porphyrins with 50/50 mixed states are those that contain $M_B M_B$. These expressions show that the strong Q-Q coupling of the $392cm^{-1}$ mode is responsible not only for the strong REP, but also for the appearance of this mode in the B(0-1) absorption band and its modest Q-B coupling for its absence in the Q(0-1) band. The size of the coupling strengths, according to this adiabatic theory, can be estimated from the Raman line heights from spectra taken with excitation in the Q(0-0) and B(0-0) bands. For example, we have shown[9,10] that the Raman line heights for Q(0-0) excitation are proportional to the Q-B coupling parameter for that mode divided by the mode frequency. Thus the strong A_{1g} modes at 1015, 1244, 1373 and $1572cm^{-1}$ seen in Figure 3 provide the coupling to the $392cm^{-1}$ mode, since it is the only one that has sufficient Q-Q coupling (as evidenced by the strong line intensity in a spectrum taken with excitation near the Soret band, Figure 3, curve A) to produce such a strong shifted excitation profile. In addition, the Raman scattering at $E_Q+392cm^{-1}$ is reduced by an interference term since the intermediate vibrational state is the same as the final vibrational state.

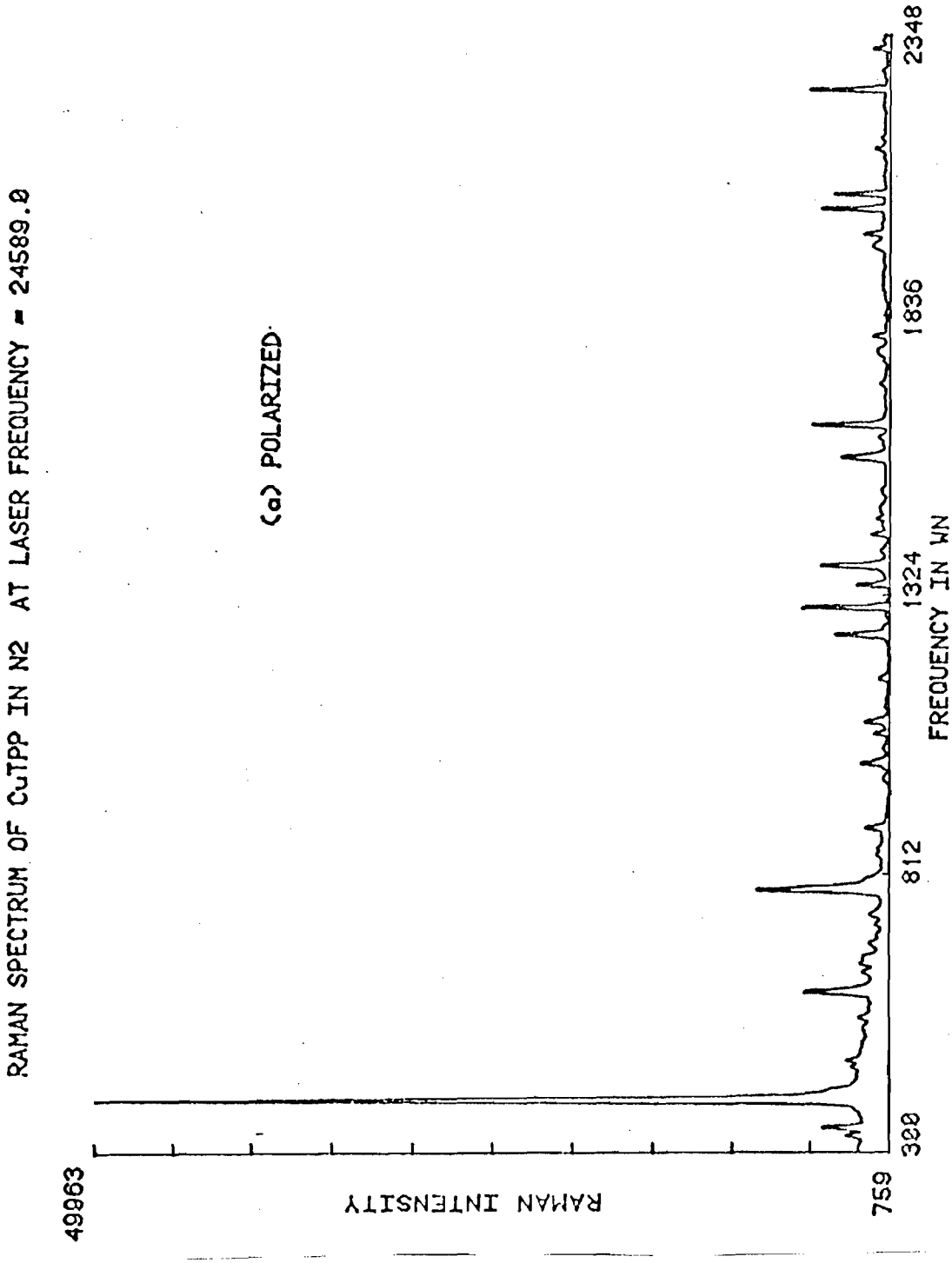


Fig. 3A. Polarized Raman spectrum of CuTPP in the vicinity of the Soret band.

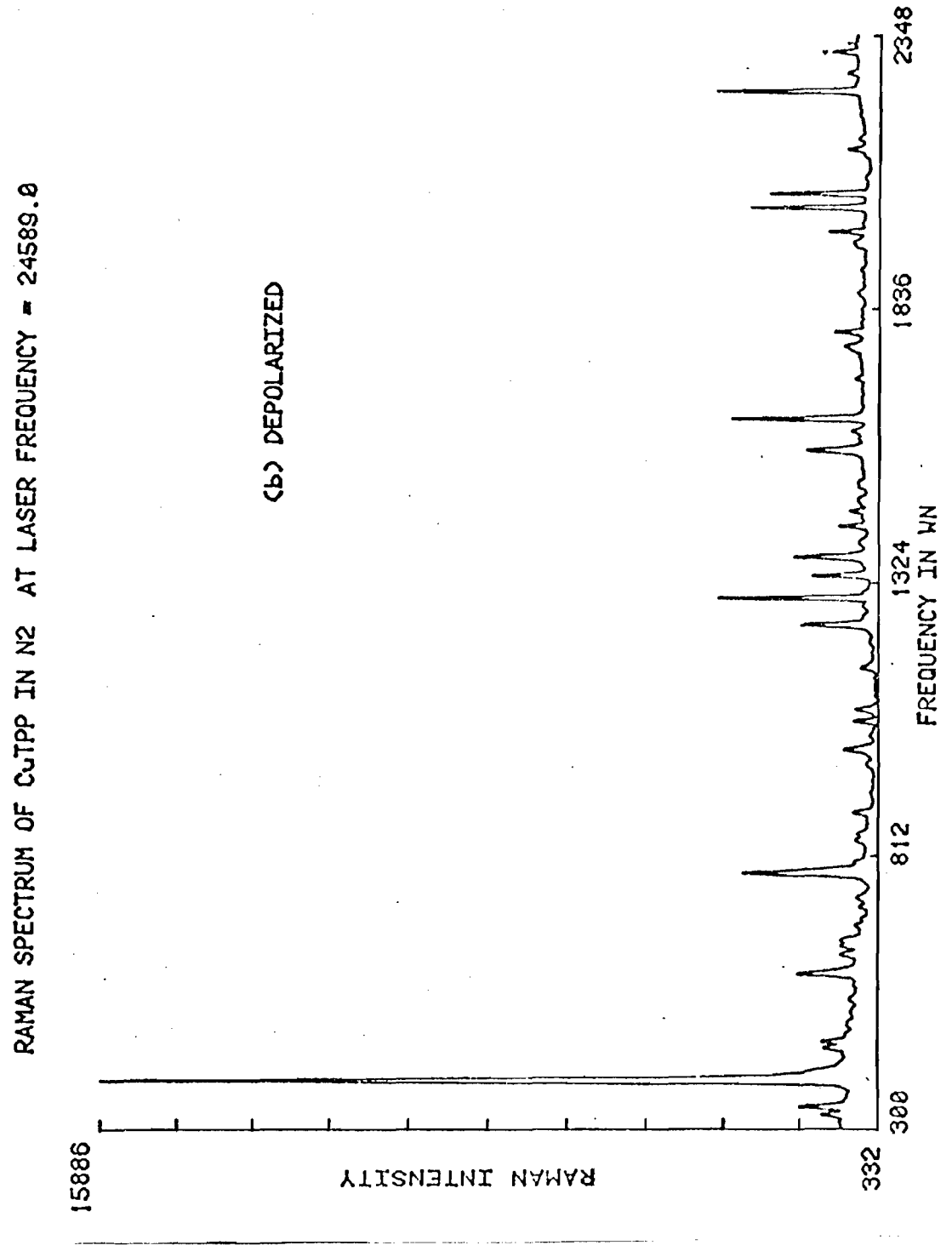


Fig. 3B. Depolarized Raman spectrum of CuTPP in the vicinity of the Soret band.

A simple theoretical framework has been developed to aid in the assignment of parameters from the experimental data. The normal coordinate shifts can be evaluated from the Raman spectrum collected at the B(0-0) excitation frequency. The effective Q to B dipole moment ratio and the Q-B energy separation can be taken directly from the absorption spectrum. The Q-B coupling strengths can be evaluated from the Raman spectrum collected at the Q(0-0) excitation frequency. The Gouterman rotation parameter can be evaluated from any B_g symmetry mode after the coordinate shift and the Q-B coupling strength for this mode are known.

The strong coupling effects found in the Raman excitation profiles of CuTPP are found to arise from third order terms involving the coupling integrals. These third order terms are present in all porphyrins but are generally small when compared to the first order effects. However, for CuTPP the Q state dipole moment is very small. In the Q state, the first order coupling terms are proportional to the Q state dipole moment, while the third order terms are proportional to the B state dipole moment. Therefore the third order terms can be of the same magnitude as the first order terms. Strong coupling is not a scattering mechanism of itself, but the absence of scattering by more familiar mechanisms.

The parameter set for CuTPP has been assigned using the Raman excitation profiles and the absorption spectrum for CuTPP in a nitrogen matrix. The set of parameters is consistent with the data for the frequency and intensity distribution of the A_{1g} symmetry mode Raman lines. The frequency distribution of the B_{1g} symmetry mode in the spectrum is accurately predicted, but the Q(0-0) to Q(0-1) intensity ratio for the Raman spectra are not. This discrepancy is due in part to difficulties encountered in collecting a complete set of reproducable Raman data throughout the Q band region. Another

possible source of error is the non-adiabatic correction applied to the vibronic states. This factor was calculated from a first order perturbation theory and may be underestimated. However, the accuracy that is observed for the A_{1g} modes indicates that the non-adiabatic correction is not too far wrong.

There are several unexplained observations. The temperature shift of the prophyrin Q band is interesting. (This shift affects only the Q band, not the B band.) While there are some mechanisms available to shift the band to higher frequencies as temperature increases, it is difficult to see how it could shift the band to lower frequencies. The matrix induced shift of the B band is also intriguing. This shift affects only the B band. Possibly the most interesting unexplained observation is the appearance in both the Q band and the B band of Raman lines whose depolarization ratio is 1/4. If the molecule truly has D_{4h} symmetry the only symmetry types of mode which could have this depolarization ratio is A_{1g}. However, if the dipole moment of the molecule is restricted to lie in the plane, the depolarization ratio for A_{1g} vibrations is 1/8. Therefore the appearance of these modes may indicate coupling of the in plane orbitals with out of plane copper d orbitals.

The expressions derived for the intensity of Raman lines could be programmed into any microcomputer to generate theoretical Raman excitation profiles and absorption spectra. The details of these profiles are extremely sensitive to the sign and magnitude of the coupling parameters. Parameter values obtained as outlined in the discussion section could be refined by fitting the theoretical Raman excitation profiles and absorption spectra with suitable experimental data. There are no miracles, though. If a molecule shows sufficient Jahn-Teller coupling, we must return to standard matrix diagonalization procedures.

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II. Publications

"Simple alignment procedure for the assembly of three-plate birefringent filters for tunable dye lasers", S. M. Mudare and D. C. O'Shea, Applied Optics 22, 640 (1983).

"Instrumentation for Resonance Raman Spectroscopy", S. M. Mudare, P. E. O'Rourke and D. C. O'Shea, submitted to Journal of Raman Spectroscopy.

III. Abstract of Thesis by Patrick E. O'Rourke

The Raman excitation Profiles of copper Tetraphenylporphyrin in a Nitrogen matrix were constructed from 152 Raman spectra collected throughout the Q band region. Absorption spectra of CuTPP in six environments were also collected to assess their effects on the molecule. A Born-Huang non-adiabatic perturbation theory is derived for porphyrins which can explain the strong coupling behavior exhibited by this data. It is found that the third order terms in the Raman scattering tensor are responsible for the strong coupling effects. This occurs not because the third order terms are abnormally large, but because the first and second order Q band scattering terms are very small for CuTPP.

IV. Scientific Collaboration

Dr. Shrikrishna Mudare, research scientist. Now at Dept. of Chemistry, University of Colorado.

Patrick E. O'Rourke, research scientist at Savannah River Laboratories of E. I. Dupont.